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Determination of Ca, Mg, Na, K in Precipitation Samples by Inductively Coupled Argon Plasma-Emission Spectrometry

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ABSTRACT

Precipitation samples can be analyzed directly for Ca, Mg, Na and K using a heated spray chamber with desolvation as the sample introduction system for ICAP. The detection limits are 0.003, 0.015, 0.006, 0.015 mgL^{-1} for Ca, Mg, Na and K respectively.

RÉSUMÉ

On peut doser directement le Ca, le Mg, le Na et le K dans des échantillons de précipitation, en utilisant une enceinte de pulvérisation chauffée munie d'un dispositif de désolvatation comme système d'introduction de l'échantillon dans le plasma d'argon à couplage inductif (ICAP). Les limites de détection sont 0,003, 0,015, 0,006 et 0,015 $mg.L^{-1}$ pour le Ca, le Mg, le Na et le K respectivement.

Management Perspective

This report completes the technology transfer from the Analytical Methods Division to the National Water Quality Laboratory of methodology for the determination of Ca, Mg, Na and K in precipitation samples by inductively coupled argon plasma (ICAP). The data presented in this joint report indicates that there is no significant difference between data generated by ICAP and atomic absorption spectrometry (Ca, Mg) and flame photometry (Na,K). The advantage of the ICAP methodology is that the four elements are determined simultaneously rather than sequentially resulting in increased efficiency and economy for the operational laboratory.

Perspective de la direction

Le présent rapport complète le transfert technologique, de la Division des méthodes analytiques au Laboratoire national de la qualité de l'eau, de méthodes de dosage du Ca, du Mg, du Na et du K dans des échantillons de précipitation, par spectrométrie en plasma d'argon à couplage inductif (ICAP). Selon les données présentées dans ce rapport mixte, il n'y a pas de différence significative entre les données obtenues par spectrométrie ICAP et celles obtenues par spectrométrie d'absorption atomique (Ca, Mg) et par photométrie de flamme (Na, K). Les méthodes ICAP sont plus avantageuses, car les quatre éléments sont dosés simultanément plutôt qu'un à la suite de l'autre; elles permettent donc aux laboratoires qui les utilisent d'être plus efficaces et de diminuer le coût des analyses.

INTRODUCTION

In recent years work has been carried out in these laboratories in developing methodology for the determination of metals in environmental samples by inductively coupled argon plasma-emission spectrometry (ICAP). Much of this work has been directed to the determination of heavy metals at sub microgram per litre levels in natural fresh waters. The approach that has been followed is the development of sample addition systems that deliver large amounts of the sample into the plasma.

Two addition systems that have been developed to date are a heated spray chamber (1)(2) and an ultrasonic nebulizer (3) both using desolvation (see Appendix A and B). The heated spray chamber system has proven to be reliable and reproducible. However, when analyzing surface waters for heavy metals at environmental levels it is necessary to obtain some preconcentration in the 'total metal' digestion step in order to obtain adequate detection limits. With hard waters there is a matrix effect since as the total solids increase the resulting aerosol becomes more difficult to transport into the plasma. The ultrasonic nebulizer system gives better sensitivity and a reduced matrix effect but the necessary equipment is not yet available for routine analysis in the National Water Quality Laboratory (NWQL).

Precipitation samples to date have been analyzed in regional laboratories of the Water Quality Branch (WQB) for the soluble 'major' ions Ca, Mg, Na and K by atomic absorption spectrometry (Ca, Mg) and

flame photometry (Na, K). Extractable heavy metals (Cd, Cu, Fe, Pb, Zn) have been analyzed by atomic absorption spectrometry (AAS). The intention is to carry out these analyses in the NWQL using ICAP.

In the present work the heated spray chamber system has been modified to give about twice the sensitivity previously reported (1) and the procedure has been optimized for the alkali metals Ca, Mg, Na and K. It has been shown that with these changes it is feasible to analyze precipitation samples for these four metals without any preconcentration step.

EXPERIMENTAL SECTION

Apparatus

The equipment is similar to that previously described (1). The modified spray chamber - desolvation equipment is shown in Figure 1. The positioning of the nebulizer in the end of the spray chamber is important. For maximum sensitivity the nebulizer is pointed down and to one side (about 10°) of the centre line of the chamber. This gives a swirling motion to the nebulizer spray.

Procedures

The samples are aspirated directly into the spray chamber. An off-peak measurement is done to establish the zero for each sample,

an on-peak measurement determines the reading for each sample. Each of these measurements is made with an integration time of 30 seconds. The ICAP forward power is 1400 watts, no helium is used in the cooling flow, the observation height is about 3 mm above the top of the R.F. coil. The sample is aspirated for 2 minutes with a 30 second wash between samples.

RESULTS AND DISCUSSION

Method Optimization

The heated spray chamber system as originally developed (1) used a laminar carrier flow through the drying chamber. More recently it was realized that there was better mass transfer and heat transfer in this chamber with tangential carrier flow. This flow pattern is achieved by inducing swirl in the spray chamber by positioning the nebulizer off-centre. With this minor change the amount of sample reaching the plasma is approximately doubled. The desolvation condenser used in the present method is similar to that developed for the ultrasonic nebulizer system (3). This is more robust than the two separate condensers previously used (1) and the reduced dead volume gives a somewhat reduced wash-out time.

ICAP Operation

When determining trace metals such as lead and cadmium we have found it preferable to use a small very 'hot' plasma and it is partly to achieve this type of plasma that the helium is added to the cooling argon flow (1). For alkali metals, however, the greatest sensitivity is achieved with a cool plasma, the signals increase going up the plasma from the RF coil. Hence, in the present method, the RF power is 1400 watts and helium is not used in the cooling flow. The viewing height used is a compromise between a higher position for the maximum potassium emission and a lower position for increased emission by magnesium.

Detection Limits

The detection limits are calculated as previously described (1). With a 30 second integration the detection limits are 3, 15, 6 and 15 μgL^{-1} respectively for Ca, Mg, Na and K.

Matrix Effects

The dissolved solids in the precipitation samples are sufficiently low that there are no observed matrix effects. The samples are aspirated as-is to the nebulizer and calibration of the system is done with standard solutions of the four metals of interest.

Method Comparison

Thirty-five precipitation samples were analyzed for Ca, Mg, Na and K by the present method. The same samples were analyzed by AAS for Ca and Mg and by flame photometry for Na and K. Each of these analyses was repeated on another day. The results of these paired analyses are shown in Tables 1 and 2. The mean differences and the standard deviations of these paired determinations for each element and method are shown in Table 3. From these it is concluded that there are no significant differences between the results obtained by ICAP and the current AAS and flame photometer methods.

It should be noted that, although these analyses are described as being 'soluble' determinations, it has not been the practice in the AAS and FP determinations to filter the samples, but rather to decant the liquid from a settled sample. For the sake of continuity this has also been done in the ICAP measurements.

LITERATURE CITED

1. Goulden, P.D. and D.H.J. Anthony, Anal. Chem. 1982. 54:1678-1681.
2. Goulden, P.D. and D.H.J. Anthony, NWRI Contribution No. 51-AMD-3-82-PDG, 1982.
3. Goulden, P.D. and D.H.J. Anthony, Anal. Chem. 1984. 56:2327-2329.

TABLE 1. Ca, Mg Analysis by ICAP and AAS

Sample	Calcium mg L^{-1}				Magnesium mg L^{-1}			
	ICAP		AAS		ICAP		AAS	
	1	2	1	2	1	2	1	2
1	0.040	0.040	N.D.*	0.03	0.001	0.001	N.D.	0.01
2	0.062	0.063	N.D.	0.03	0.062	0.071	0.05	0.05
3	0.15	0.15	N.D.	0.08	0.024	0.021	0.01	0.02
4	0.051	0.064	N.D.	0.03	0.002	0.006	N.D.	0.01
5	0.050	0.046	0.05	0.45	0.046	0.039	0.01	0.05
6	0.067	0.069	N.D	0.02	0.009	0.001	N.D.	0.01
7	0.22	0.23	0.06	0.18	0.023	0.030	0.02	0.03
8	0.48	0.53	0.36	0.40	0.077	0.076	0.06	0.06
9	0.89	0.86	0.71	0.74	0.085	0.073	0.09	0.07
10	0.31	0.33	0.16	0.23	0.032	0.051	0.03	0.04
11	0.13	0.13	N.D.	0.13	0.001	0.002	N.D.	0.02
12	0.52	0.53	0.52	0.52	0.087	0.089	0.09	0.08
13	0.13	0.12	N.D.	0.07	0.038	0.014	0.01	0.02
14	0.27	0.25	0.13	0.20	0.040	0.029	0.03	0.03
15	0.18	0.18	0.03	0.12	0.035	0.021	0.01	0.03
16	0.21	0.22	0.14	0.19	0.011	0.011	0.01	0.02
17	0.12	0.17	0.01	0.10	0.015	0.012	N.D.	0.01
18	0.13	0.12	N.D.	0.10	0.026	0.023	0.01	0.03
19	0.23	0.24	0.15	0.21	0.41	0.39	0.39	0.33
20	0.21	0.20	0.19	0.21	0.050	0.059	0.06	0.06
21	0.062	0.063	0.04	0.04	0.003	0.009	0.01	0.02
22	0.37	0.35	0.44	0.44	0.72	0.70	0.86	0.91
23	0.70	0.72	0.96	1.03	1.7	1.7	2.26	2.45
24	0.23	0.20	0.22	0.23	0.12	0.10	0.13	0.14
25	0.18	0.25	N.D.	0.01	0.001	0.002	N.D.	0.01
26	0.033	0.036	0.02	0.01	0.029	0.016	0.02	0.03
27	1.15	0.18	0.13	0.12	0.12	0.10	0.13	0.12
28	0.056	0.066	0.06	0.04	0.046	0.047	0.05	0.05
29	0.27	0.27	0.42	0.43	0.039	0.041	0.07	0.06
30	0.49	0.50	0.73	0.74	0.066	0.074	0.13	0.12
31	0.13	0.11	0.15	0.09	0.012	0.028	0.02	0.02
32	0.28	0.29	0.32	0.29	0.031	0.039	0.05	0.05
33	0.050	0.087	0.05	0.01	0.001	0.001	N.D.	N.D.
34	0.036	0.039	0.06	0.02	0.002	0.002	N.D.	N.D.
35	0.043	0.052	0.05	0.03	0.002	0.002	0.01	0.01

*N.D. - Not Detected, these are values less than 0.05 mg L^{-1} for Ca and 0.01 mg L^{-1} for Mg. All ICAP values are reported even if they are less than the detection limit.

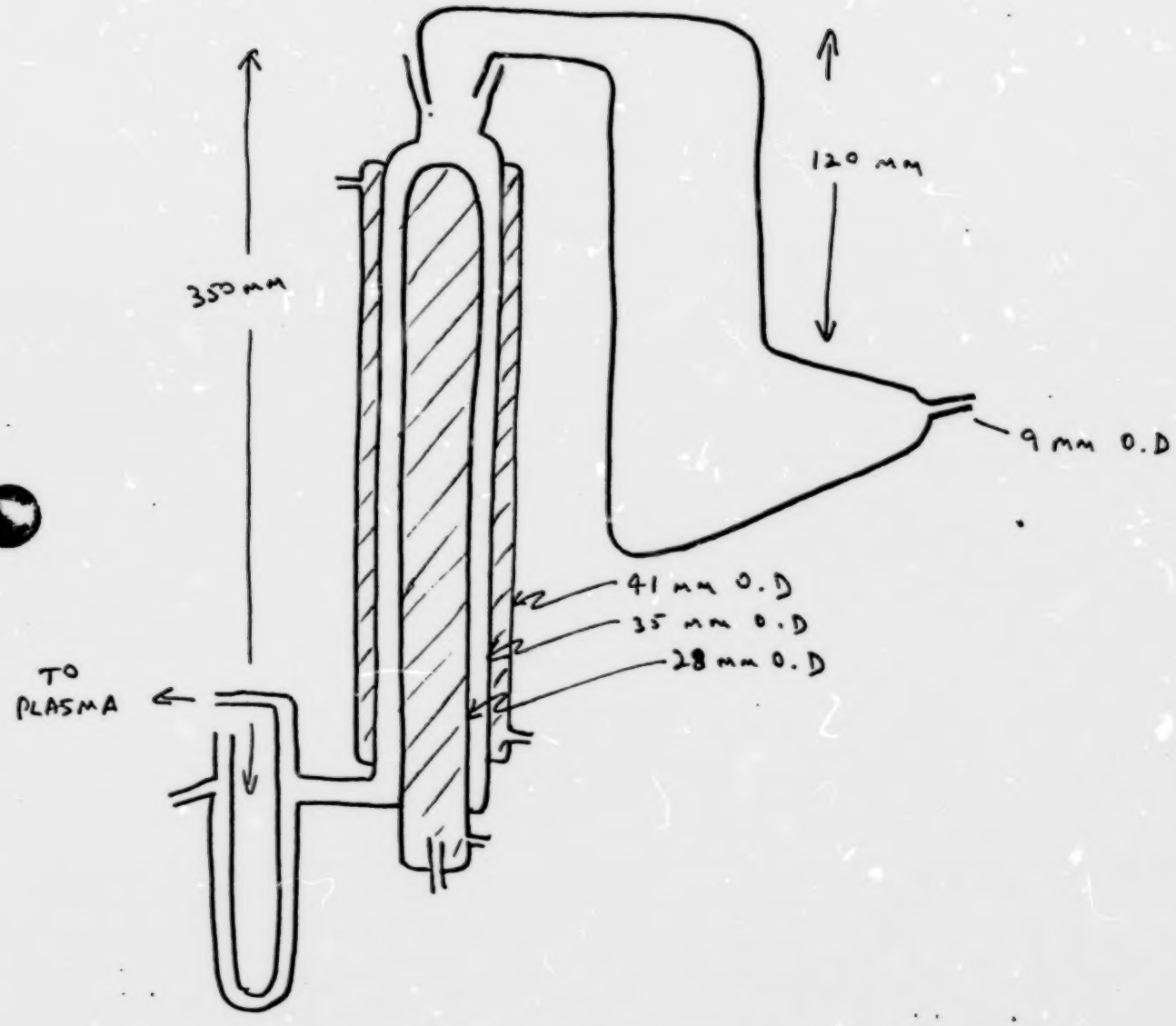
TABLE 2. Na, K. Analysis by ICAP and Flame Photometry

Sample	Sodium mg L^{-1}				Potassium mg L^{-1}			
	ICAP		Flame Phot.		ICAP		Flame Phot.	
1	0.10	0.099	0.09	0.10	0.031	0.014	N.D.*	0.03
2	0.57	0.57	0.47	0.49	0.081	0.090	0.02	0.04
3	0.18	0.14	0.09	0.11	0.14	0.094	0.05	0.07
4	0.086	0.078	0.07	0.09	0.027	0.014	0.01	0.02
5	0.30	0.28	0.18	0.35	0.079	0.071	0.05	0.08
6	0.24	0.22	0.14	0.21	0.031	0.017	N.D.	0.02
7	0.055	0.056	0.06	0.07	0.020	0.021	0.02	0.03
8	0.069	0.066	0.05	0.07	0.039	0.035	0.02	0.04
9	0.085	0.088	0.09	0.09	0.078	0.077	0.10	0.10
10	0.044	0.070	0.04	0.06	0.005	0.010	0.01	0.02
11	0.21	0.24	0.23	0.29	0.032	0.060	0.04	0.06
12	0.17	0.16	0.14	0.14	0.039	0.050	0.06	0.06
13	0.22	0.21	0.13	0.13	0.033	0.017	0.01	0.02
14	0.073	0.075	0.07	0.07	0.049	0.029	0.03	0.03
15	0.34	0.39	0.11	0.23	0.029	0.025	0.04	0.03
16	0.13	0.14	0.14	0.13	0.030	0.042	0.06	0.05
17	0.088	0.13	0.07	0.09	0.005	0.010	0.02	0.02
18	0.17	0.17	0.17	0.17	0.021	0.005	0.03	0.03
19	2.9	2.7	2.94	3.07	0.019	0.021	0.11	0.13
20	0.48	0.49	0.48	0.54	0.060	0.060	0.06	0.08
21	0.38	0.33	0.27	0.32	0.006	0.004	0.01	0.02
22	7.7	7.5	7.77	7.71	0.30	0.33	0.30	0.29
23	21.3	18.5	19.64	20.13	0.85	0.67	0.76	0.75
24	0.86	0.81	0.96	1.02	0.072	0.072	0.08	0.10
25	0.12	0.15	0.07	0.08	0.020	0.005	0.01	0.01
26	0.38	0.35	0.28	0.28	0.031	0.005	0.02	0.02
27	1.0	1.1	1.10	1.12	0.085	0.082	0.06	0.06
28	0.52	0.53	0.53	0.54	0.026	0.035	0.02	0.02
29	0.20	0.25	0.25	0.27	0.064	0.083	0.06	0.10
30	0.16	0.17	0.26	0.29	0.063	0.071	0 09	0.12
31	0.35	0.17	0.11	0.12	0.039	0.071	0.02	0.04
32	0.20	0.21	0.24	0.22	0.034	0.052	0.06	0.06
33	0.79	0.80	0.10	0.07	0.007	0.010	0.01	0.01
34	0.20	0.25	0.19	0.21	0.022	0.057	0.01	0.02
35	0.23	0.24	0.19	0.19	0.005	0.014	0.01	0.01

*N.D. - Not Detected, these are values less than 0.02 mg L^{-1} for Na and K.

TABLE 3. Standard Deviations and Mean Differences for Replicate Analyses

	Calcium	Magnesium	Sodium	Potassium
	mg L^{-1}			
AAS-FP Replicates				
Standard Deviation	0.0624	0.0259	0.0685	0.0122
Mean Difference	0.0547	0.0168	0.0454	0.0132
ICAP Replicates				
Standard Deviation	0.022	0.0107	0.0476	0.0340
Mean Difference	0.0186	0.0101	0.0362	0.0236
ICAP/AAS-FP Pairs				
Standard Deviation	0.0602	0.0187	0.0313	0.0147
Mean Difference	0.0487	0.0108	0.0279	0.0113



SPRAY CHAMBER - DESOLVATION EQUIPMENT

FIGURE 1

Determination of Trace Metals in Freshwaters by Inductively Coupled Argon Plasma Atomic Emission Spectrometry with a Heated Spray Chamber and Desolvation

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A modified spray chamber, where the spray escaping from the chamber is heated to produce a stable aerosol, is used to determine total trace metals in freshwaters. With a 10-fold preconcentration in the digestion process, the detection limits obtained ranged from 3 $\mu g\ L^{-1}$ for Al to 0.6 $\mu g\ L^{-1}$ for Pb to 0.03 $\mu g\ L^{-1}$ for Mn.

Atomic emission spectrometry using excitation in an inductively coupled argon plasma (ICAP), with its capability for simultaneous multielement determination, is a very useful technique for the analysis of wastewaters. However, for relatively unpolluted natural water such as the open waters of the Great Lakes, the technique as commonly used is not sufficiently sensitive to determine most of the trace metals of interest in this laboratory, namely, Al, Cd, Co, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, and Zn. Methods to improve the detection limit which have been used are changes in the nebulizer, such as the use of an ultrasonic nebulizer (*1*, *2*) and the use of a heated spray chamber (*3*). In the present work these options were investigated and it was found that a modified spray chamber, where only the portion of the spray that escapes from the chamber is heated, provides an increase in sensitivity over the conventional spray chamber of about a factor of 10. The detection limit is improved by a factor of 5. The equipment is easy to construct and operate and this technique is presented as another option for the determination of trace metals by ICAP. It is being used for the analysis of natural waters for total trace metals with particular emphasis on waters from the Great Lakes. By combination of this technique with a 10-fold concentration in the sample digestion step the detection limits of the above metals range from 0.03 $\mu g\ L^{-1}$ for manganese to 0.6 $\mu g\ L^{-1}$ for lead and 3 $\mu g\ L^{-1}$ for aluminum. Simultaneously with the trace metals determination, the major ions in the sample, namely, Ca, Mg, Sr, Ba, Na, and K are also determined.

EXPERIMENTAL SECTION

Apparatus. The flow through the system is shown schematically in Figure 1. The sample is pumped to a nebulizer in the spray chamber; the spray escaping from the conical section is heated in the cylindrical portion of the chamber. The resulting aerosol is cooled in the two condensers, where most of the water separates out, and the desolvated aerosol is passed to the torch in the ICAP system.

When used in the automated mode a Sampler IV (Technicon Corp.) is used. The pump is a pump I (Technicon Corp.). Between the pump and the nebulizer is 1 m of AWG 30 "Teflon" spaghetti tubing to act as a pulse suppressor. The nebulizer is a concentric glass nebulizer. Nebulizers from E. Meinhard Associates have been used and also nebulizers of the same type made in this laboratory. The modified spray chamber is made from a 125-mL conical flask to which is joined a piece of glass tubing, 45 mm o.d. The dimensions are shown in Figure 2, also shown is the arrangement of the desolvation condensers. The heater for the cylindrical chamber is made from aluminum sheet (as shown in Figure 2) and in this shroud is placed a quartz–halogen lamp (Cole Parmer, Catalog No. C-3151-30). This lamp is a 600-W, 115 V ac lamp and 55 V is applied to it through a variable transformer.

Table I. Analytical Wavelengths and Detection Limits

element	wavelength, nm	order	detection limits, $\mu g\ L^{-1}$: conventional spray chamber	detection limits, $\mu g\ L^{-1}$: present method
Al	308.22	2	17	2.9
Cd	226.50	3	0.16	0.047
Co	238.89	2	2.0	0.31
Cr	267.72	2	1.4	0.27
Cu	324.72	2	2.8	0.57
Fe	259.94	2	1.1	0.19
Mn	257.61	2	0.16	0.026
Mo	202.03	2	1.4	0.28
Ni	231.60	2	1.5	0.30
Pb	220.35	3	2.0	0.59
V	311.07	2	1.0	0.22
Zn	213.86	3	0.31	0.067
Ba	455.40	1	1.3	0.24
Ca	317.93	2	2.0	0.36
K	766.49	1	46	4.8
Mg	279.08	2	4.7	0.97
Na	589.00	1	25	4.6
Sr	407.77	1	0.16	0.03

The torch used is similar to that previously described (*4*), it uses 17 mm bore silica tubing for the outer tube. The spraying and desolvation equipment are mounted on the bench beside the torch chamber. The aerosol is carried to the torch through a 3 mm i.d. glass tube, connected to the base of the torch with a short length of silicone rubber tubing to allow the torch to be positioned. The ICAP system is an Applied Research Laboratory ICP torch compartment with a Model No. QA-137 spectrometer as previously described (*4*). The analytical wavelengths used are given in Table I.

The tubes used for evaporation and digestion of the samples are of UV grade silica, 23 mm o.d. and 170 mm long. A forced air oven at 180 °C is used to evaporate the samples; an aluminum hot block is used for the acid digestion. The antibumping system used in the oven consists of a manifold connected to a nitrogen cylinder. To the manifold are attached numerous pieces of AWG 30 Teflon tubing, each 35 cm long.

Reagents. Ultrapure nitric acid (Ultrex, J. T. Baker Chemical Co.) was used for sample preservation and in the sample digestion procedure. Metals standards were prepared from 1000 mg L^{-1} atomic absorption standards (Fisher Scientific Co.).

Procedures. *Sample Pretreatment.* The samples are preserved by acidifying them to 0.2% (v/v) with concentrated nitric acid. About 35 g of a well-shaken sample is added to a silica tube. The tube is placed in a rack in the oven, the Teflon tube is inserted, and the nitrogen pressure is adjusted so that about 1 mL min^{-1} is blown into the liquid. The sample is evaporated to about 2 mL and 0.5 mL of concentrated nitric acid is added. The tube is transferred to the aluminum hot-block and the solution evaporated to near dryness. One milliliter of water is added and the solution is evaporated to dryness. This is repeated twice. The solid is dissolved in a mixture of 0.35 mL of concentrated nitric acid and 1 mL of water (heating this solution may be required in some cases) and the weight is made up to 3.5 g. (The original sample and final dilution are measured by weighing the tube, to

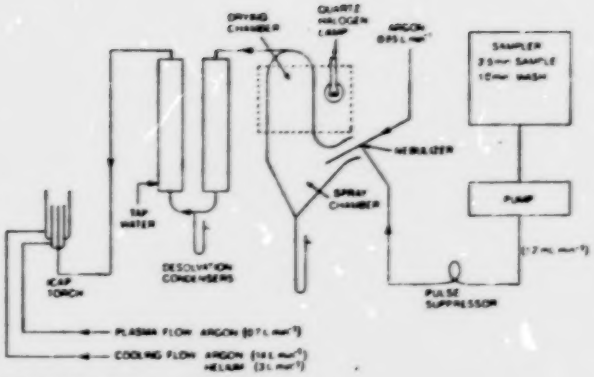

Figure 1. Flow-through system.

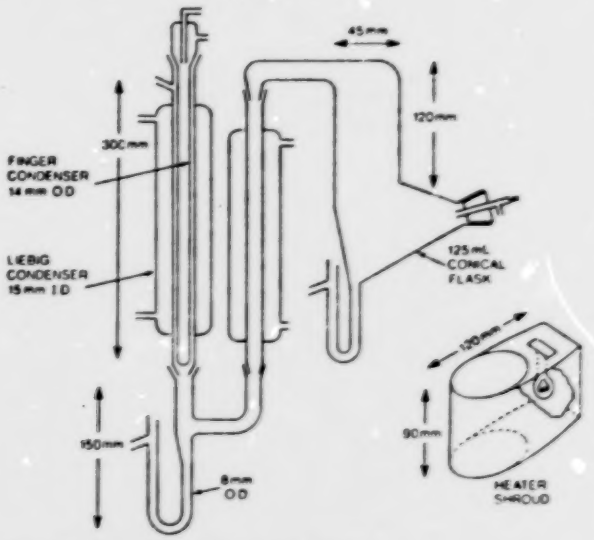

Figure 2. Spray chamber and condensers.

avoid any transfer except from sample bottle to tube and to minimize contamination.) The concentrated sample is then analyzed in the ICAP system. Dilution factors are calculated from the weights and the measured specific gravities of matrix-matched standards.

ICAP Analysis. The ICAP system is set in operation with 0.2% HNO_3 being pumped through the nebulizer. The heating lamp is turned on and when conditions have stabilized, which takes about 30 min, the samples and standards are pumped to the spray chamber. The operating conditions are as follows: observation height, 2 mm above top of rf coil; plasma forward power, 1600 W; plasma reflected power, less than 10 W; argon cooling flow, 14 L min^{-1}; helium cooling flow 3 L min^{-1}; argon plasma flow, 0.7 L min^{-1}; nebulizer gas flow 0.85 L min^{-1}; nebulizer liquid flow, 1.2 mL min^{-1}; lamp power, 180 W (55 V). The calibration of the instrument is made with a matrix-matched solution containing 1 mg L^{-1} of each of the metals or by the addition of 1 mg L^{-1} of each of the metals to selected samples. The zero for each standard and sample is determined by making measurements "off-peak" by moving the spectrometer primary slit. The wavelength shift used is 0.023 nm below the peak for the elements measured in the third order, 0.034 nm for those measured in the second order. The off-peak and on-peak measurements are made with a 50-s integration time. The sample is aspirated for 2.5 min, between each sample is used a 1-min wash of 0.2% HNO_3.

RESULTS AND DISCUSSION

Method Optimization. *Spray Chamber.* The purpose of the spray chamber is to allow a large fraction of the small drops produced in the spray to escape to the vertical chamber where they will be dried by the radiant heat from the lamp bulb. The rationale is that the dried particles are much lighter than the corresponding drops of solution and will produce an abundant and stable aerosol.

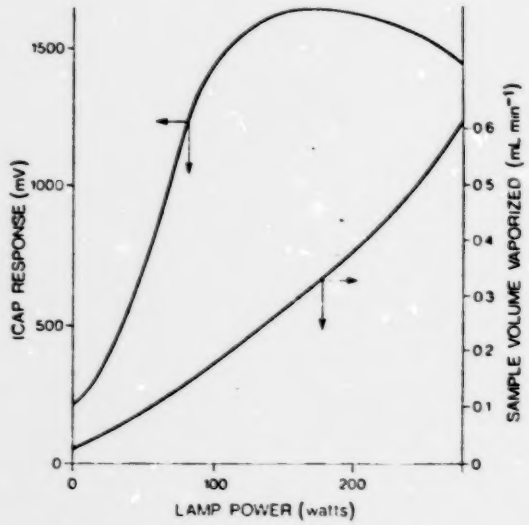

Figure 3. Effect of lamp power.

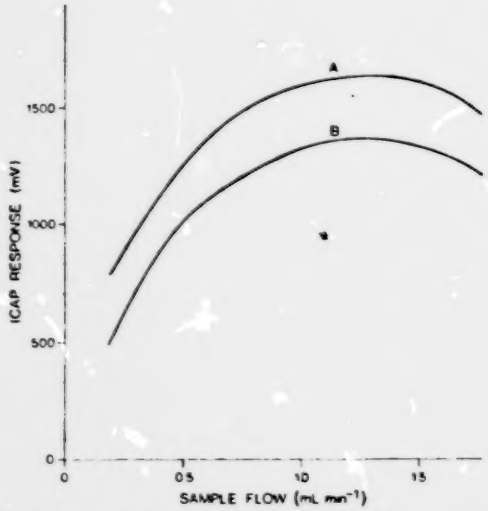

Figure 4. Effect of sample flow: (A) lamp power 180 W; (B) lamp power 100 W.

The dimensions of the spray chamber were investigated, they were changed to give volumes from about 50 to 500 mL using a variety of shapes. It was found that the 125-mL conical flask gave the best performance. The diameter of the cylindrical portion was varied over the range of 10–57 mm, it was found that a diameter of about 45 mm was the optimum. It is postulated that at the smaller diameters less spray escapes into the chamber and at the larger diameters the gas velocity is insufficient to keep the particles suspended.

The effects of the various operating parameters were studied. The effect of lamp power is shown in Figure 3. This shows the signal given in the manganese channel and the amount of water that is vaporized from the spray chamber as the lamp power is changed. This is for a sample flow to the nebulizer of 1.2 mL min^{-1} of a solution containing 1 mg L^{-1} manganese. It is seen that while the amount of water that is vaporized from the chamber increases steadily with lamp power, there is an optimum power for the signal from the plasma. The effect of sample flow to the nebulizer is shown in Figure 4. The other metals give results similar to those shown for manganese.

Table II. Effect of Ca, Mg, and Na Levels on Sensitivity

amt of Ca, mg L^{-1}	amt of Mg, mg L^{-1}	amt of Na, mg L^{-1}	rel sens
0.0	0.0	0.0	1.00
7.2	1.6	2.0	0.93
18.0	4.0	5.0	0.91
36.0[a]	8.0[a]	10.0[a]	0.87
72.0	16.0	20.0	0.80
180.0	40.0	50.0	0.73
360.0	80.0	100.0	0.66

[a] Approximate composition of Niagara River water.

The efficiency of the system in delivering sample to the plasma torch was determined in two ways. The first of these was to connect an automated system for generating arsine (*3*) to the plasma in parallel with the spray–dry system. Standard solutions of arsenic were fed alternately through the two systems and the signals compared. This enabled the efficiency of the spray system to be compared directly with that of the arsine-generation system. The other measure made was to filter out the aerosol from the gas stream. It was found that a 10-μm "Mitex" filter (LCWP 02500, Millipore Corp.) would remove essentially all of the aerosol. The material caught in the filter was dissolved and the concentration of the trace metals determined. There was excellent agreement between the two methods. In summary, at the optimum shown in Figure 3, i.e., at 180 W, 9% of the 1.2 mL min^{-1} of sample pumped to the nebulizer is transferred to the torch.

The cycle of 2.5 min sample with a 1 min wash gives a plateau lasting 120 s in which the "on-peak" and "off-peak" readings may be taken.

ICAP Operation. It was found that the best definition of what was the "zero" in the analysis was the off-peak measurement. With some of the lines used there were some N–O emission bands that were in the off-peak region. This problem has been discussed by Wallace (*5*) who used an extended torch to shield the plasma from the air. We attempted to avoid these bands by using such an extension and by using an outer tube around the torch and shielding it with argon or helium. We found however that with the torch shielded from the air, the plasma expanded in length and the signals decreased. The best solution that we found for this N–O problem was to increase slightly the cooling flow in the torch and make the measurements at a lower portion in the plasma before the air could diffuse into the plasma. In this position the background is higher than in the normal analytical region but on balance it was found the best position for us. The use of a gas such as hydrogen or helium added to the cooling flow, as described by Horlick (*6*), also "shrinks" the plasma and results in higher signals. The extra gas flow also helps shield the plasma from the air diffusion.

Sample Pretreatment. In the methods used in this laboratory for total trace metals by atomic absorption spectrophotometry, the evaporation and digestion procedures are carried out in borosilicate flasks. Aluminum is leached from the glass under these conditions so that a determination of total aluminum in natural water is impossible. It is to overcome this problem that the silica tubes are used in the digestion process. With these tubes for the analysis of deionized water, which allows a much higher concentration factor than lake waters, there was found to be no contamination of the samples by metals leaching from the tubes. It is estimated that if any leaching of the metals had occurred to give levels one-tenth of those shown in Table I as the "present system" detection limits, it would have been detected in these tests.

Matrix Effects. It is found that there are no spectral interferences nor any effects on the plasma from the large amounts of the major ions such as calcium, magnesium, sodium, and potassium, that are in the concentrated lake water samples. However, it is found that as the dissolved solids content of the sample increases, less of the sample reaches the plasma. This is presumably because of the different physical properties of the particles during the spraying, drying, and transfer process. The result is that as the dissolved solids level increases, the sensitivity for all the metals decreases. The magnitude of this effect is shown in Table II where the plasma response is given for various calcium, magnesium and sodium concentrations in the solution aspirated. (The "relative sensitivity" in this table is calculated from the total millivolt signal in the 12 trace metal channels; the individual metal responses are all similar.)

It is seen that at 36 mg L^{-1} Ca, 10 mg L^{-1} Na, and 8 mg L^{-1} Mg concentration (which is approximately the composition of the waters from the Niagara River) there is 87% of the

Table III. Typical Results on Niagara River Sample by Present Method and AAS

element	present method[a] mean[b]	present method[a] std dev[c]	found AAS, μg L^{-1}	present method, sample spiked, μg L^{-1} spike	found	spike	found	spike	found
μg L^{-1}									
Al	72.5	1.1	73.6	6.0	77.4	15.0	88.4	30	101.8
Cd	0.052	0.011	0.042	0.1	0.13	0.25	0.31	0.5	0.58
Co	0.21	0.12	0.13	0.6	0.74	1.5	1.78	3.0	3.04
Cr	0.52	0.11	0.64	0.6	1.21	1.5	1.87	3.0	3.62
Cu	3.5	0.17	3.7	1.2	4.81	3.0	6.43	6.0	10
Fe	86.7	0.64	88.3	0.4	87.5	1.0	87.9	2.0	88.1
Mn	2.84	0.020	2.90	0.06	2.91	0.15	3.02	0.3	3.20
Mo	0.95	0.090	0.73	0.6	1.43	1.5	2.34	3.0	4.07
Ni	1.56	0.15	1.43	0.6	2.27	1.5	3.31	3.0	4.74
Pb	0.59	0.24	0.90	1.2	1.91	3.0	3.82	6.0	6.74
V	0.32	0.090	0.46	0.4	0.82	1.0	1.24	2.0	2.46
Zn	1.42	0.026	1.34	0.14	1.60	0.35	1.94	0.7	2.06
Ba	10.6	0.14							
Sr	141.0	0.52							
mg L^{-1}									
Ca	44.4	0.62							
K	1.34	0.020							
Mg	8.14	0.17							
Na	10.9	0.10							

[a] In μg L^{-1} for Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, Ba, and Sn. In mg L^{-1} for Ca, K, Mg, and Na. [b] Mean of five replicates. [c] Standard deviation.

response for a distilled water matrix. At the 10-fold concentration of these river water samples the response obtained is 66% of that of a distilled water matrix. Hence, there is actually a times 7.6 increase in sensitivity obtained by the 10-fold concentration of these waters. It was confirmed that this is due to less sample reaching the plasma and not due to effects on the plasma of the higher solids content of the analytical stream carrying out efficiency-of-sample-transfer measurements as described above.

Because of this effect it is necessary that the instrument be calibrated with a standard that is matrix-matched to the sample. In this laboratory, this gives no hardship when analyzing batches of similar samples since the major ions are determined as part of the water quality measurements. Matching the matrix with Ca, Mg, Na, and K also serves to provide standards for the determination of these four major ions. Where it is more convenient than matching the matrix, a replicative sample can be processed with a standard addition of the 12 trace metals to give a level of 1 mg L^{-1} of each in the concentrated sample. It has been confirmed by making several standard additions to a variety of samples that in these lake waters, the calibration "curve" is sufficiently linear for a single "high" point calibration to be satisfactory. When "strange" samples are analyzed, standard additions are made at three levels to check that the calibration is linear.

It should be noted that the effect of the matrix concerns only the slope of the calibration line, the "zero" for each sample is determined by the off-peak reading taken as the sample is aspirated.

Detection Limits and Sensitivity. The variance of the readings obtained in each of the analytical channels was determined both short term, i.e., over a few minutes elapsed time, and long term, i.e., over several hours of operation, in a manner similar to that previously described (*4*). This was done by using a synthetic lake water sample at the "zero" level of trace metals. It was found that there was no significant difference between these two measures of the variance and that the readings were normally distributed about their mean. This was true for both the on-peak and off-peak readings; it was further shown that the variances in the on-peak and off-peak readings were not different. Then over several days of operation, for each element was calculated a single value that represented the common variance in the on-peak and off-peak signals (approximately 400 readings were used to calculate this common variance).

Since the result obtained in the analysis is from the difference between the on-peak and off-peak readings, the variance in this is twice the variance calculated above. The detection limit, the lowest level that, with a single determination, gives a signal that is statistically greater than the zero, is 1.645 $(2^{1/2})\ \sigma A^{-1}$ where 1.645 represents the "Z" value at a 95% confidence level, σ is the standard deviation from the above variance, and A is the sensitivity expressed as the signal (in mV) per $\mu g\ L^{-1}$ in the sample.

Compared to a conventional spray chamber, the modified system gives a sensitivity (A) increase of about 10, while the variance is increased by about 4 (σ is increased by 2). This results in an improvement in the detection limit of a factor of about 5. The detection limits obtained with the two systems are shown in Table I. Both of these sets of detection limits were derived as described above.

The "major" ions, Ca, Mg, Ba, Sr, Na, and K are determined at the same time as the trace metals. The analytical wavelengths and detection limits for these elements are also shown in Table I. (For Ca, Mg, and Na, the detection limits were determined with a water matrix.)

Water Samples. The method has been applied to many water samples taken from the Great Lakes. For many of these samples the results were compared with those by chelation–solvent extraction–atomic absorption spectrometry. These comparisons in all cases gave good agreement. Several of the lake water samples were spiked with the 12 trace metals at levels of approximately twice, five times, and ten times the detection limit levels shown in Table I. Analysis of the spiked samples gave recovery of the spikes within the statistical expectations. In Table III is shown a typical set of results obtained for a water samples from the Niagara River. The sample was analyzed five times, the mean results are given together with the results obtained by AAS and the results of the spiking experiment.

The N.B.S. Standard Reference Material 1643a (trace elements in water) was analyzed and there was excellent agreement with the certified values.

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APPENDIX B

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Modified Ultrasonic Nebulizer for Inductively Coupled Argon Plasma Atomic Emission Spectrometry

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Stable and high efficiency operation of an ultrasonic nebulizer is achieved when both the sample and the cooling water are properly coupled to the transducer. In the horizontal configuration this is achieved by ensuring that no air bubbles can remain trapped in the cooling water beneath the transducer and that the sample wets the upper surface of the nebulizer.

Ultrasonic nebulizers used for sample introduction in analysis by inductively coupled argon plasma (ICAP) spectrometry are typified by those described by Olsen et al. (*1*) and by Taylor and Floyd (*2*) in which the ultrasonic transducer is mounted with its face in a vertical (*1*) or horizontal (*2*) position. Although having several advantages over conventional pneumatic nebulizers, these ultrasonic systems do not seem to have gained general acceptance in ICAP analysis. Our experience has been that the equipment as described (and purchased) has problems with both long- and short-term stability. We found that while the nebulizers would produce copious quantities of fine aerosol, on many occasions, within a few minutes or perhaps the next day, the amount of aerosol would be drastically reduced for no reason apparent to us. Discussions with other workers in the field suggest that that was a typical experience. We, therefore, developed a pneumatic nebulizer/heated spray chamber technique (*3*) for routine analysis of freshwater samples. This technique, which also involves a 10-fold preconcentration step, has proven to be a reliable and reproducible way to determine trace elements in freshwater. However, the physical properties of the dried aerosol change as the total solids content of the sample solution increases so that at high total solids levels the amount of sample reaching the plasma is drastically reduced. This makes the technique unsuitable for such samples as seawater and digested sediment and fish samples. We find the ultrasonic nebulizer to be much less subject to this type of matrix effect. This is presumably because of the different particle size distributions in the aerosol from the two nebulizers, although we have made no particle size measurements. Hence, if the ultrasonic nebulizer could be made to operate in a stable and reproducible manner, it would broaden the range of environmental sample types that could be conveniently analyzed by ICAP.

In the present work some causes of instability in the operation of the ultrasonic nebulizer have been identified. We find that minor modifications in the construction and operation of the commonly used equipment give a system suitable for routine analysis of all of our environmental samples. Compared to the heated spray chamber, the short-term (i.e., within 1 day) stability is better and the long-term (i.e., week to week) reproducibility is at least as good.

The nebulizer produces a large volume of aerosol, and the heated chamber–condenser system used with the pneumatic nebulizer would not properly desolvate it. Desolvation equipment with a greater capacity was therefore built to handle this large volume of aerosol.

EXPERIMENTAL SECTION

Apparatus. Figure 1 shows the construction of the transducer assembly. The transducer is a piezoelectric disc type (Channel Products Inc., Model CPMT) operating at a nominal frequency of 1.4 MHz. The transducer, 26.5-mm diameter, is bonded to a glass disc, 27.0-mm diameter. The glass tube to hold the transducer is standard wall borosilicate glass, 28-mm o.d. The end of this tube is expanded and ground with a "glass-joint" taper so that when the transducer is inserted in it there is a lip 2 mm high around it. The glass disc is bonded to the tube with acoustic epoxy cement ("Eccobond 55"). The rf power for the transducer is generated with a frequency synthesizer/function generator (Hewlett-Packard, Model 3325A) amplified with an rf amplifier (ENI, Model 2100L). Reflected power is monitored with an rf directional wattmeter (Bird "Thruline", Model 43).

The sample is pumped with a peristaltic pump (Gilson, Minipuls). Delivery of the sample to the nebulizer is made via Teflon standard wall tubing (size, AWG No. 22). This delivers the sample to the outer edge of the glass disc inside the lip. The precise position is not important; it makes no difference whether or not the end of the tube touches the glass.

The desolvation equipment is shown in Figure 2. The wet aerosol is dried in an annular chamber heated with a quartz-halogen lamp (CGE Model DYH) at its center. The power to the lamp is supplied through a variable transformer. The resulting water vapor is removed in the condenser in tandem with the drying chamber. The ICAP system is as previously described (*3*).

Reagents. The reagent was 0.01% (by volume) solution of a surfactant (Rohm and Haas, Triton X-405).

Procedure. The sample flow rate is 3.0 mL/min^{-1}; the carrier gas flow rate is 850 mL/min^{-1}. A sample is pumped for 2.5 min; between each sample is interspersed a 1-min wash of 0.2% HNO_3. Integration times are 50 s "on-peak" and 50 s "off-peak". These are the same conditions as those previously described (*3*). The power applied to the transducer is 40-W forward power with less than 1-W reflected power. The heating lamp is operated at 250 W (70 V). The plasma operating conditions are the same as those previously described (*3*).

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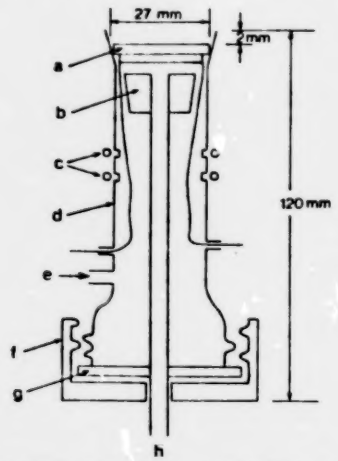

Figure 1. Transducer assembly: a, transducer; b, No. 3 rubber stopper; c, "O" rings; d, 28-mm-o.d. borosilicate tubing; e, cooling water in; f, 38–430 screw cap; g, silicone rubber seal; h, cooling water out.

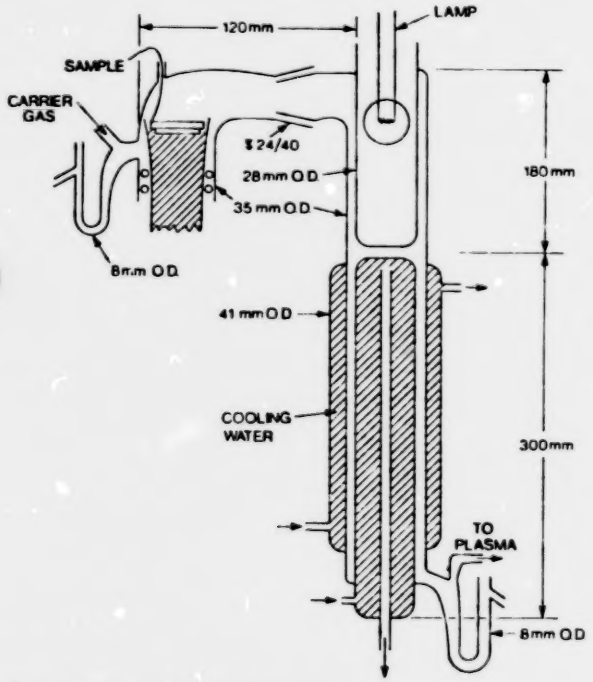

Figure 2. Drying–desolvation apparatus.

Each day, before samples are analyzed, the surfactant wash solution is pumped over the transfucer surface for 10 min.

RESULTS AND DISCUSSION

Method Optimization. Transducer Operating Stability. For routine use in ICAP analysis, the most important requirement of the ultrasonic nebulizer is that it produce continuously a large and stable amount of aerosol over the analytical period and that the rate and stability of that production be reproducible from day to day. This ability is influenced by the electromechanical stability of the transducer and is related to the efficiency of coupling between the transducer and the medium adjacent to each face, i.e., sample on one side, cooling water on the other. Stable operation of the transducer is achieved only when both faces are uniformly covered with liquid. Instability, as shown by erratic fluctuations of forward and reflected power in the rf circuit, produces variations in aerosol production and in ICAP response.

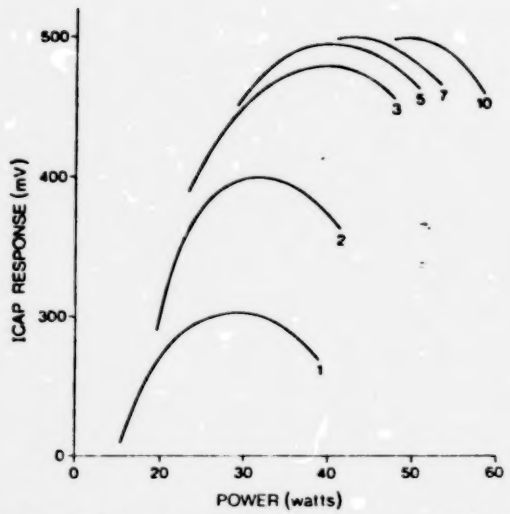

Figure 3. ICAP response at various transducer power levels and sample flow rates. (Figures on each curve are flow rates in mL·min^{-1}.)

If the transducer is completely immersed in water under "high-flow" conditions so that the temperature is controlled and no bubbles of air can collect on the surfaces, it will operate for many days with no variation in the forward and reflected power levels. If air bubbles are allowed to collect on either of the surfaces, the power levels fluctuate as the air bubbles grow and then break free.

In the vertical configuration used by Olsen et al. (*1*), the cooling water side of the transducer can be kept free from bubbles but it is impossible to maintain a uniform water film on the sample side. In the horizontal configuration used by Taylor and Floyd (*2*), the sample side can be uniformly wetted but there are problems with air bubbles collecting at the bottom surface of the transducer. These bubbles arise both from air bubbles brought in with the cooling water and from dissolved air released through the cavitation produced by the transducer motion. This problem is overcome in the present system by passing a large volume of cooling water (about 0.5 L/min^{-1}) through the narrow space between the rubber stopper and the transducer. The all-glass construction makes it possible to adjust the thickness of this space and monitor how effective it is in preventing the collection of bubbles.

The ground surface of the glass disc on the transducer as supplied (by Channel Products Inc.) is rough enough that, if it is clean, water will wet it satisfactorily. However, after use, the surface becomes contaminated with grease, from either the equipment or the samples, and it is no longer completely wetted. This results in erratic operation of the transducer. If the glass surface is washed with a surfactant solution, the surface remains wettable for some considerable time, depending on the samples being analyzed. The samples we analyze are mostly clean water from the Great Lakes. With these samples it is sufficient (and convenient) to wash the transducer glass surface each day as part of the start-up procedure. The Triton X-405 surfactant was at hand and proved satisfactory. We have not investigated other surfactants.

The sample flow rate and the power applied to the transducer must also be balanced in order to keep a water film on top of the nebulizer. For any particular sample rate there is a power minimum below which a standing wave is formed and no aerosol is produced. As the power is increased, aerosol begins to be formed; as the power is increased further, a point is reached at which the sample is thrown off the surface so violently that dry spots occur. At this point the transducer operation becomes unstable and the ICAP response decreases

Table I. Detection Limits with Ultrasonic Nebulizer

element	detection limit, $\mu g \cdot L^{-1}$	element	detection limit, $\mu g \cdot L^{-1}$
Al	5.1	Mn	0.042
Cd	0.091	Mo	0.50
Co	0.55	Ni	0.46
Cr	0.42	Pb	0.94
Cu	0.91	V	0.35
Fe	0.35	Zn	0.12

because the dry spots are alternately formed and then covered with sample. The relationship between power and ICAP response for various sample flow rates is shown in Figure 3. The ICAP response shown is the reading in the manganese channel. The responses for other metals were similar. It is seen that at each flow rate there is an optimum power level and that the optimum response increases with sample flow rate up to about 7 $mL \cdot min^{-1}$. We attribute the flattening of response at the higher flow rate to the inability of the desolvation system to transport the aerosol. The sample flow rate and power levels of 3.0 $mL \cdot min^{-1}$ and 40 W, respectively, were chosen as representing an acceptable ICAP response with extended transducer life.

DRYING AND DESOLVATION

A large amount of aerosol is produced by the nebulizer. Under the "routine analysis" conditions (3 $mL \cdot min^{-1}$, 40 W) approximately 0.5 $mL \cdot min^{-1}$ of water leaves the nebulizer chamber and is collected via the condenser system. From measurements similar to those previously described (*3*), we estimated that the equivalent of 0.3 $mL \cdot min^{-1}$ of sample reaches the plasma under these conditions. We believe that the largest potential loss of aerosol is by agglomeration of the wet particles. The small volume nebulizer chamber and the annular drying chamber permit the rapid removal and drying of the particles to minimize this agglomeration. The condenser provides fast and efficient condensing of the water vapor with a minimum of dead volume. The volumes of the nebulizer chamber, drying chamber, and condenser are 26, 25, and 35 mL, respectively. These small dead volumes also give fast sample washout characteristics; e.g., when a sample containing 1 $mg \cdot L^{-1}$ of manganese is followed by a 0.2% HNO_3 wash, the ICAP signal falls to 1% of the sample reading within 30 s of the changeover.

SENSITIVITY AND DETECTION LIMITS

The detection limits of the system were determined in a manner similar to that previously described (*3*). The detection limits observed for a number of elements in water from Lake Ontario as is, i.e., with no preconcentration, are shown in Table I. These are about 6 times better than those obtained with the pneumatic nebulizer/heated spray chamber system. The improvement is caused by a 3-fold increase in sensitivity and a 4-fold reduction in the variance; i.e., the standard deviation of replicate analyses decreased by a factor of 2.

This lower variance obtained with the ultrasonic nebulizer, as compared to the pneumatic nebulizer/heated spray chamber system, is a measure of the greater stability of the nebulizer within the analytical period of a day. The long term stabilities of the two systems are about the same. Analyses carried out on the same standards over a period of 3 months give "millivolt readings" that do not vary by more than 10% for either of the systems.

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